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Isotope Effects in Switchable Metal-Hydride Mirrors

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Measurements of optical reflectance, transmittance, and electrical resistivity on the switchable mirror systems YH_x and YD_x show that the absorption of hydrogen induces the same variations as that of deuterium. In both cases there is a weak transparency window for the metallic dihydride (dideuteride) phase and a yellowish transparency in the insulating trihydride (trideuteride) phase. The slightly higher electrical resistivity of the deuterides is related to the lower energy of their optical phonons. The absence of significant isotope effects in the optical properties of YH_x (YD_x) is at variance with Peierls-like theoretical models. It is, however, compatible with strong electron correlation models.

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Spectacular changes in the optical and electrical properties were recently discovered [1,2] in metal-hydride films of yttrium and lanthanum near their metal-insulator transition: the dihydrides are excellent metals and shiny while the trihydrides are insulators and transparent in the visible part of the optical spectrum. The metal-insulator (MI) transition from a shiny to a transparent state is reversible and simply induced at room temperature by changing the surrounding hydrogen gas pressure or electrolytic cell potential [3–5]. All trivalent rare-earth hydrides and even some of their alloys exhibit switchable optical and electrical properties [4,6]. In the transparent state they have characteristic colors: for example, YH_3 is yellowish, LaH_3 red, while some alloys are colorless. These films can therefore be used as switchable mirrors.

Soon after their discovery it was realized that the insulating state of the switchable mirrors could probably not be understood in terms of existing one-electron theories, since Wang and Chou [7,8] and Dekker *et al.* [9] had concluded a few years earlier from self-consistent band structure calculations, that YH_3 was a semimetal with, in fact, a very large band *overlap* (1.5 eV). By minimizing the total energy, these authors found that the HoD_3-($P\bar{3}c1$)-type structure was energetically more favorable than the cubic BiF_3-type structure originally assumed by Switendick [10]. By allowing for Peierls-like displacements of the hydrogen atoms near the metal planes, Wang and Chou [8] found that the total energy could be further lowered by an extra 30 meV per YH_3. They finally obtained an electronic band structure with only one electron band and one hole band crossing the Fermi energy E_F near the center of the Brillouin zone. The total density of states at E_F is small and the hole and electron densities are approximately 5×10^{26} m^{-3}. This value is, however, still much larger than the value $\lesssim 10^{24}$ m^{-3} expected for stoichiometric YH_3 on the basis of an extrapolation of our Hall measurements for $YH_{2.886}$-$YH_{2.911}$ [11]. The predicted semimetallic character is also not consistent with the existence of an optical gap of 2.8 eV [4].

These difficulties stimulated theorists to reconsider the YH_x and LaH_x systems. Somewhat similarly to the situation for high-T_c superconductors, two clearly different lines of thought have been proposed so far: Peierls-like band structure models and strongly correlated electron models.

(i) Strong electron correlation: Already in 1995 Sawatzky [12] suggested that electron correlation effects might explain the existence of the large optical gap in YH_3. Along the same lines Ng *et al.* [13,14] discuss the MI transition in LaH_x starting either from the metallic LaH_2 or the insulating LaH_3. Addition of hydrogen into the octahedral interstitial sites of LaH_2 introduces spin $1/2$ magnetic impurities which couple to the conduction $5d$-lanthanum electron spins. In this Kondo insulator model conduction electrons are captured by the neutral hydrogen to form tightly bound singlets. Conversely, removal of hydrogen from the octahedral sites of the insulating LaH_3 leaves a vacancy which effectively donates an electron to the conduction band. This electron is, however, expected to be so strongly localized (the radius of the vacancy state is estimated to be about 0.3 nm in contrast to typically 10 nm in standard semiconductors) that an impurity band can form only at a very high doping level of about 20% impurities. Eder *et al.* [15] introduce a further ingredient in the theory. They show that the strong dependence of the hydrogen $1s$ orbital radius on the occupation number (the radius of the $1s$ orbital is about 3 times larger for the H^- ion than for the neutral H atom) leads to the formation of localized singlet bound states involving one electron on the hydrogen and one on the neighboring metal orbitals. This is similar to the Zhang-Rice singlet [16] proposed for the high-T_c superconductors, but with the new ingredient of the breathing hydrogen orbital leading to a strong occupation number dependence of the electron hopping ("breathing Hubbard model").

(ii) Band structure approach: Following the idea that small but symmetry lowering displacements of the hydrogen atoms can induce a band gap, Kelly *et al.* [17] determined the ground state of YH_3 using the

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Car-Parrinello method. From density functional calculations within the local density approximation they found a new broken-symmetry ($P3$) structure with a direct gap of 0.8 eV. As calculations based on the local density approximation systematically underestimate band gaps by about 1 eV [18], the value of 0.8 eV obtained by Kelly *et al.* was considered as being consistent with experimental data.

So far no consensus has been reached and even additional models have been proposed to explain the insulating state of YH_3 [19] and LaH_3 [20,21].

Recent high precision neutron powder diffraction (NPD) data, obtained by Udovic *et al.* [22], showed no experimental evidence for the broken-symmetry ($P3$) structure proposed by Kelly *et al.* Even after a close reexamination of the spectra, Udovic *et al.* [23] conclude that the HoD_3 structure is preserved.

Kelly *et al.* reply in Ref. [24] by giving several reasons why the proposed symmetry breaking should not be dismissed based only on the NPD data. First, they mention that *thin films* of YH_3 may behave differently compared to bulk YH_3, because strains in the film caused by substrate clamping can have a large influence on the equilibrium structure of a lattice. However, the neutron diffraction data obtained by Remhof *et al.* [25] on thin monocrystalline films are still consistent with the HoD_3 structure and show no evidence for the broken symmetry ($P3$) structure. Moreover, our experiments on both *polycrystalline* and *epitaxial* YH_x films of various thicknesses [5,26,27] have shown no essential differences in optical and electrical behavior, indicating that the insulating state of YH_3 is insensitive to clamping strains.

The other arguments in Ref. [24] are all based on the fact that the zero point motion of the H(D) atoms is comparable to the symmetry breaking H(D) displacements. According to Kelly *et al.* [17] the total energy difference between the metallic HoD_3 and the $P3$ structure is 11.7 meV per YH_3. This is smaller than the 57 meV of the optical phonon modes in YH_3 [28] corresponding to the motion along the c axis of the metal- and near-metal-plane H(D) atoms, the atoms mainly responsible for the energy lowering in the $P3$ structure. This implies that the ground state of $YH_x(YD_x)$ is a superposition of the insulating broken-symmetry state ($P3$ structure) and the metallic high-symmetry state (HoD_3 structure). In YD_3, the aforementioned optical phonon energies are $\approx$16 meV lower than in YH_3 [29]. Therefore a large isotope effect is expected.

In this Letter we show that no significant isotope effect is present in $YH_x(YD_x)$. The behavior of the optical reflectance, transmittance, and electrical resistivity upon H(D) loading is essentially the same in YH_x (YD_x). The very small differences observed in our measurements are difficult to understand within the approach of Kelly *et al.* However, the absence of any sizable isotope effect is consistent with models based on strong electron correlation effects.

Pairs of Y films of 50 nm thickness are evaporated simultaneously under UHV conditions (10^{-9} mbar) on a quartz substrate (Suprasil 1, Heraeus) by means of an e-gun. After deposition of a 10 nm protecting Pd layer they are transferred to a Bruker IFS 66/S FTIR spectrometer. During $H_2(D_2)$ gas loading at 190 Pa, transmittance and reflectance spectra are measured alternately ($0.72\ \text{eV} < \hbar\omega < 3.5\ \text{eV}$) and at the same time the resistivity ρ of the film is measured continuously using the *Van der Pauw* method. After stabilization of the optical reflectance, transmittance, and resistivity, the $H_2(D_2)$ gas pressure is increased in steps to 10^5 Pa. The H(D) concentration x in $YH_x(YD_x)$ is determined by linking the measured resistivity ρ with $x(\rho)$ as measured using the electrochemical method described by Kooij *et al.* [5]. Figure 1 shows the reflectance and transmittance as a function of x, after the film has been put in contact with H_2 gas at room temperature. In the dihydride phase ($x \approx 2$), the reflectance has a minimum for $\hbar\omega = 1.96$ eV. At low photon energies the film is highly reflective due to the free electrons (intraband absorptions). The (screened) plasma energy of YH_2 is 1.64 eV [30], explaining the sharp decrease of the reflectance around this energy. The reflectance at higher energies is caused by interband absorptions from the conduction band into higher d-derived bands as was shown by Peterman *et al.* [31]. As a result, there is neither a strong reflectance nor a strong absorption at intermediate photon energies, giving rise to the transmittance window in Fig. 1(a), with a maximum at $\hbar\omega = 1.80$ eV. With increasing x, the low energy reflectance decreases because more and more free electrons are bound by the additional hydrogen atoms. Finally, the transparent trihydride state is reached, having an absorption edge at $\approx$2.8 eV, which gives $YH_{3-\delta}$ its typical yellow color.

The central result of this work is the absence of fundamental differences between the optical properties of YH_x and YD_x (see Figs. 1 and 2). To put this in evidence more clearly, some representative reflectance

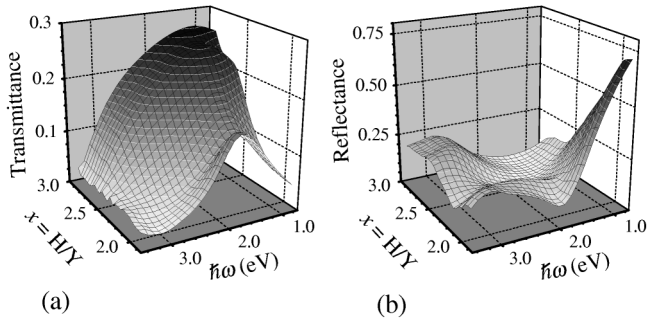

FIG. 1. Hydrogen concentration dependence of the optical transmittance (a) and reflectance (b) versus hydrogen concentration x of a 50 nm thick YH_x film protected by a 10 nm Pd layer. The film is loaded at room temperature in a H_2 atmosphere. The concentration x is determined electrochemically [5].

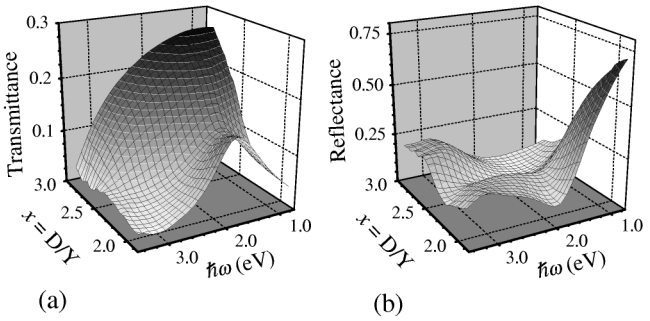

FIG. 2. As in Figs. 1(a) and 1(b), but now for a film loaded in a D_2 atmosphere. This film was deposited simultaneously with the film in Fig. 1.

and transmittance spectra of YH_x and YD_x are compared in Fig. 3. Each spectrum is labeled by the value of the electrical resistivity measured simultaneously with the optical properties.

It turns out that, for all spectra, $\rho(YD_x)$ is somewhat larger than $\rho(YH_x)$. The H(D) concentration dependence of the resistivity, as determined electrochemically, is shown in Fig. 4. Although the resistivity of YD_x is systematically higher than that of YH_x, the important point is that the qualitative behavior for both materials is the same. The larger resistivity of YD_x is due to the fact that the optical phonon energies in YD_x are $\approx\sqrt{2}$ times lower than those in YH_x [29]. Therefore at a given temperature more optical phonons are excited in the deuteride than in the hydride, resulting in a larger phonon contribution to the electrical resistivity.

From a detailed analysis of the maxima near $\hbar\omega = 3.1$ eV in the optical reflectance spectra for $x_{H(D)} > 2.7$, we find that $YD_{3-\delta}$ has an optical gap which is $\Delta E_g = 35 \pm 13$ meV larger than for $YH_{3-\delta}$. This difference can be understood in terms of the electron correlation approach used by Ng *et al.* for LaH_3. The gap E_g^{H}, respectively, E_g^{D}, arises mainly through a strong Gutzwiller renormalisation of the overlap integrals of the low lying s bands and $E_g^{\mathrm{H(D)}} = E_d - E_{\mathrm{H(D)}} - W_{\mathrm{H(D)}}/2$, where E_d is the bottom of the d band, and $E_{\mathrm{H}} = E_{\mathrm{D}}$ is the center of the H(D) low lying band. Only the width $W_{\mathrm{H(D)}}$ of the H(D) bands depends on the mass $M_{\mathrm{H(D)}}$ of the interstitial H(D). As $W_{H(D)}$ depends quadratically on the zero point motion (ZPM) amplitude of H(D), the isotope effect is expected to be small. This is in strong contrast with the Peierls-like models, in which minor displacements of H atoms induce large changes in the band structure. To estimate the magnitude of the effect of the ZPM on $E_g^{\mathrm{H(D)}}$, we use the fact that $W_{\mathrm{H(D)}} \propto a^{-n}$, in which a is the distance between the metal-plane $H_m(D_m)$ atoms and the tetrahedral $H_t(D_t)$ atoms, and n is a constant depending on the symmetry of the overlapping states. With $a = a_0 + u_m + u_t$, where a_0 is the equilibrium H_m-$H_t(D_m$-$D_t)$ distance, u_m is a small displacement of the metal-plane $H_m(D_m)$ atoms, and u_t is a small displacement of the tetrahedral $H_t(D_t)$

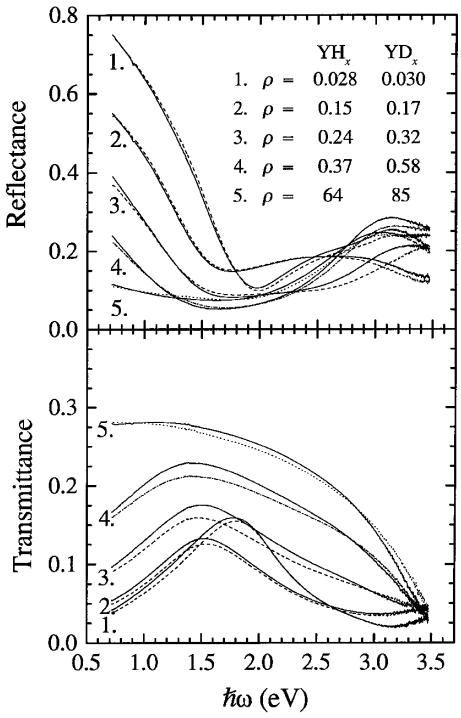

FIG. 3. Comparison of representative optical reflectance and transmittance spectra of the YH_x film (solid lines) and YD_x film (dashed lines) of Figs. 1 and 2. The electrical resistivities corresponding to each pair of similar spectra are indicated in units of $m\Omega$ cm and were corrected for the influence of the Pd caplayer using a parallel resistor model.

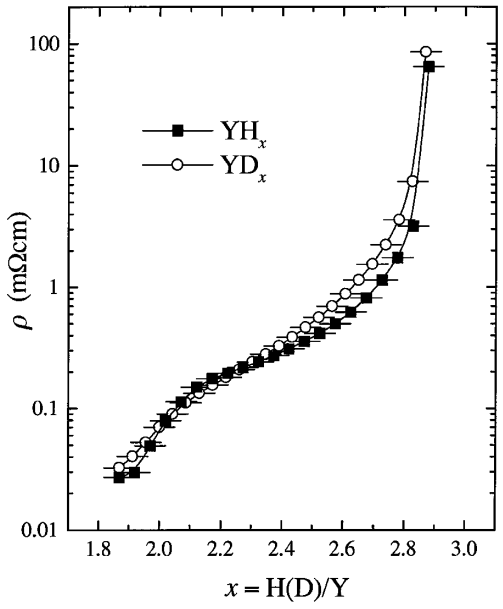

FIG. 4. Electrical resistivity $\rho(YH_x)$ and $\rho(YD_x)$ as a function of x, as determined electrochemically. The data were corrected for the influence of the Pd layer using a parallel resistor model.

atoms from their equilibrium positions, we find

$$\Delta E_g = \frac{n(n+1)W_0}{4a_0^2}\left[\langle u_{H_m}^2\rangle - \langle u_{D_m}^2\rangle + \langle u_{H_t}^2\rangle - \langle u_{D_t}^2\rangle\right],$$

in which W_0 is the width of the H(D) bands in absence of ZPM. The mean squared amplitudes of the different atoms are given by $\langle u^2\rangle = (\hbar^2/m)\sum_{i=1}^{3}(1/\hbar\omega_i)(\nu_i + \frac{1}{2})$, where m is the atomic mass, $\hbar\omega_i$ are the optical phonon energies corresponding to the vibrational modes of each atom, and ν_i is the occupation number of each mode. Using $T = 295$ K, $W_0 = 5$ eV [15], $a_0 = 2.4$ Å [22], $\hbar\omega_1 = 57$ meV, $\hbar\omega_2 = 82$ meV, $\hbar\omega_3 = 94$ meV (for H_m) and $\hbar\omega_i = 120$ meV (for H_t) [28], $\omega_H \approx \sqrt{2}\,\omega_D$ [29], $m_D = 2m_H$, and $n = 2$ (for s-s and s-p overlap integrals) [32], we find $\Delta E_g = 39$ meV, which is in agreement with the experimental value. This and the similar optical and electrical behavior of YH_x and YD_x indicate that both systems evolve in the same way during H(D) absorption. We conclude that the semiconducting nature of $YH_3(YD_3)$ is robust and unlikely to be due to a subtle rearrangement of the H(D) atoms in the Y-lattice.

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